Electronic and magnetic properties of double-impurities-doped TiO2 (rutile): First-principles calculations

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Electronic and magnetic properties of double-impurities-doped TiO_2 (rutile): First-principles calculations

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The electronic and magnetic properties of double-impurities-doped TiO_2 (rutile) are explored using first-principles calculations within the generalized gradient approximation to examine their potential use as spintronic system. Calculations are performed on all possible sets of double impurities (M_1 and M_2) from M_1=Cr, Mn, Fe, Co, and Ni, and M_2=Mo, W, and Re. The results show the overlapping of the highest occupied impurity states with the bottom of the conduction band of the host system and the half-metallic nature in Fe- and W-doped TiO_2, making them suitable as spintronic systems. These impurities preferentially substitute adjacent Ti sites and form a stable magnetic complex with oxygen atoms. © *2006 American Institute of Physics*.
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Oxide-based diluted magnetic semiconductors (DMS) are more suitable for making spintronic devices in comparison with the non-oxide-based DMS, because of their many favorable attributes including the wide band gap, higher *n*-type carrier concentration, higher transition temperature (T_c), low cost, and environmental safety.[1] Matsumoto *et al.*[2] observed ferromagnetic order in $Ti_{1-x}Co_xO_{2-\delta}$ (anatase) ($x \leqslant 0.08$) thin film grown above room temperature, with a magnetic moment of $0.32\mu_B$, per Co ion. Following this, many experimental[3,4] and theoretical[5,6] works have focused on this system to understand the origin of ferromagnetism and the role of the oxygen vacancies. In this system, the highest occupied state of Co is observed to be significantly far away from the conduction band minimum (CBM) of TiO_2 (rutile).[7,8] Our preliminary calculations also showed similar results on other single-impurities-doped TiO_2.[9] This impedes the motion of the charge carriers from the impurity states to the conduction band. Thus, there is a current interest in the development of spintronic systems, in which the impurity states lie close to CBM, to improve the efficiency of such systems. In the present paper, we suggest an alternative way of bringing the highest occupied impurity states closer to CBM by doping with double impurities, rather than increasing the carrier concentrations in system.

The double-impurities-doped systems are expected to have several advantages over the single impurity systems [Figs. 1(a) and 1(b)]. First, by the suitable choice of double impurities, it is possible to bring an energetic matching between the highest occupied impurity states and the CBM. Second, the double impurities form stable magnetic complexes with oxygen atoms (M_1-O-M_2; where M_1 and M_2 are two different impurities). Third, it is possible to avoid the oxygen vacancies in double-impurities-doped TiO_2. In the case of single impurity (say Co) doped TiO_2, oxygen vacancies arise since the stable valance states of Co are Co^{2+} or Co^{3+}, whereas Co^{4+} is rather unstable. To investigate the importance of double impurities and to predict suitable impurity pairs to dope in TiO_2 (rutile), we consider cases of 15 impurity pairs (M_1 and M_2) that are chosen from the 3*d* transition metal elements (Cr, Mn, Fe, Co, and Ni) for M_1 and 4(5)*d* elements (Mo, W, and Re) for M_2. The electronic and magnetic properties are studied using first-principles calculations.

All calculations in the present paper are performed using first-principles calculations within the generalized gradient approximation (GGA).[10] The valence electrons of all atoms used in these calculations are defined by ultrasoft pseudopotentials.[11,12] The wave functions are expanded into plane waves, with a kinetic-energy cutoff of 450 eV. A supercell [as shown in Fig. 1(c)] consisting of a $2\times2\times2$ periodic repetition of the primitive unit cell is constructed. A $4\times4\times6$ grid of *k* points is used to sample the Brillouin zone. The structural and ionic relaxations are alternatively performed on the supercell, until the atomic forces are converged to ±0.01 eV/Å. Spin-polarized calculations are also performed on the supercell.

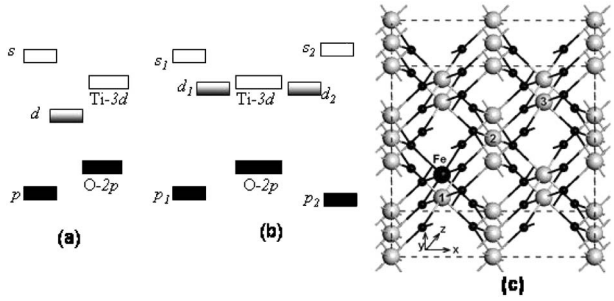

FIG. 1. (a) General representative of *s*,*p*,*d* states of the impurity atom, and Ti-3*d* and O-2*p* of single impurity doped TiO_2 (rutile) and (b) $s_{1,2}$, $p_{1,2}$, and $d_{1,2}$ are energy states of two different impurities. The occupied and unoccupied states are shown by black and white boxes, respectively. (c) Schematic diagram of relaxed geometry of Fe- and Mo-doped TiO_2. Ti, O, and Fe atoms are shown as larger gray, smaller black, and larger black balls, respectively. Three different substitutional sites for Mo (named as 1, 2, and 3 in the figure) have been selected. Based on total energy calculations, Mo is likely to be located at site 1. The energy differences between Mo in sites 2 and 3, and 1 are 0.127 and 0.164 eV, respectively.

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The concentration of double impurities is considered as 12.5% of the Ti atoms, which is slightly higher than the solubility of Co in TiO_2 anatase (~8%) (Ref. 2) since other works have reported ferromagnetic order up to impurity concentrations of 12%.[13] Further, we consider the double impurities (M_1 and M_2) substitute only in Ti sites of TiO_2 (rutile), as shown in earlier studies.[8] In the present paper, the exact locations of double impurities are obtained from the various possible combinations of the Ti sites. The results showed that the double impurities substitution of the nearest neighbor Ti sites along the z axis of rutile has the lowest energy [Fig. 1(c)]. The distance between these impurities decreases with decreasing the total energy of the system [see Fig. 1(c) caption]. It conveys that the double impurities are likely to be located at adjacent Ti sites and these interact through the O atoms.

Since there are two possible modes [ferromagnetic (FM) and antiferromagnetic (AFM)] of coupling between the double impurities, we studied both configurations (FM and AFM) for double-impurities-doped TiO_2. The most favorable configuration is obtained by comparing the total energies of two configurations. In the case of Fe- and Mo-doped rutile, the AFM coupling between these two impurities is favored with a total magnetic moment of $4\mu_B$. It is also estimated that the local moment of Fe and Mo are 3.84 and $-0.36\mu_B$, respectively. In the optimized structure, the Fe-O-Mo magnetic complex is observed, with the Fe-O, Mo-O, and Fe-Mo bond distances being 2.06, 1.95, and 2.55 Å, respectively, and the Fe-O-Mo angle being 96°. The Fe-O bond distance differs significantly from the Ti-O bond distance of 1.94 Å,[14] since the large moment of Fe atom pushes away the oxygen atoms.

The total and partial densities of states (DOS) for this system are obtained using the tetrahedron method with Blöchl corrections.[15] The partial DOS of Fe- and Mo-doped TiO_2 are shown in Fig. 2(a). It is understood that the valence and conduction bands are predominantly contributed by O-2p and Ti-3d, respectively. Also, the valence bandwidth (about 6 eV) is in agreement with the experimental results.[16] In the partial DOS of Fe-3d, the majority spin state, t_{2g}, is in the range of −5 to −2 eV. The exchange splitting between the t_{2g} states is larger than the crystal field splitting between the majority t_{2g} and e_g states, suggesting a high spin configuration for Fe. Due to crystal field splitting of the octahedrally coordinated systems, the t_{2g} state is always followed by the e_g state for both the majority (up) and the minority (down) spin states. The minority t_{2g} spin state of Fe is lying close to the Fermi level, followed by the e_g state. Similarly, a part of the minority t_{2g} state of Mo is lying below the Fermi level and all other states are located above the Fermi level. The highest occupied impurity states (of both Fe and Mo) are 0.09 eV away from the CBM. Similar calculations are extended for all the other 14 impurity pairs doped TiO_2 rutile. The separation between the highest occupied impurity states and the CBM for all these systems is given in Table I.

It is seen that the highest occupied impurity states of two impurity pairs (Fe-W and Cr-W) doped TiO_2 overlap with CBM. The partial DOS of these systems are presented in Figs. 2(b) and 2(c). In Cr-W-doped TiO_2, one of the impurity states (W-5d) overlaps with the conduction band and the other (Cr-3d) is nearly 1 eV lower than CBM. In addition, a part of both the majority and the minority states (W-5d) are simultaneously occupied, which suggest the metallic nature of this system [Fig. 2(b)]. This is quite unfavorable for fabricating the spintronic devices, since only the half-metallic nature gives rise to 100% spin polarization in the ground state.[17] In the other system (Fe-W-doped rutile), both the impurity states (Fe-3d and W-5d) are energetically matched and are also overlapped with the CBM. This leads to the delocalization of the charge carriers more efficiently than in any other double-impurities-doped TiO_2 systems. For all other impurity pairs, the energy separation between the impurity states and CBM is significantly far away from the

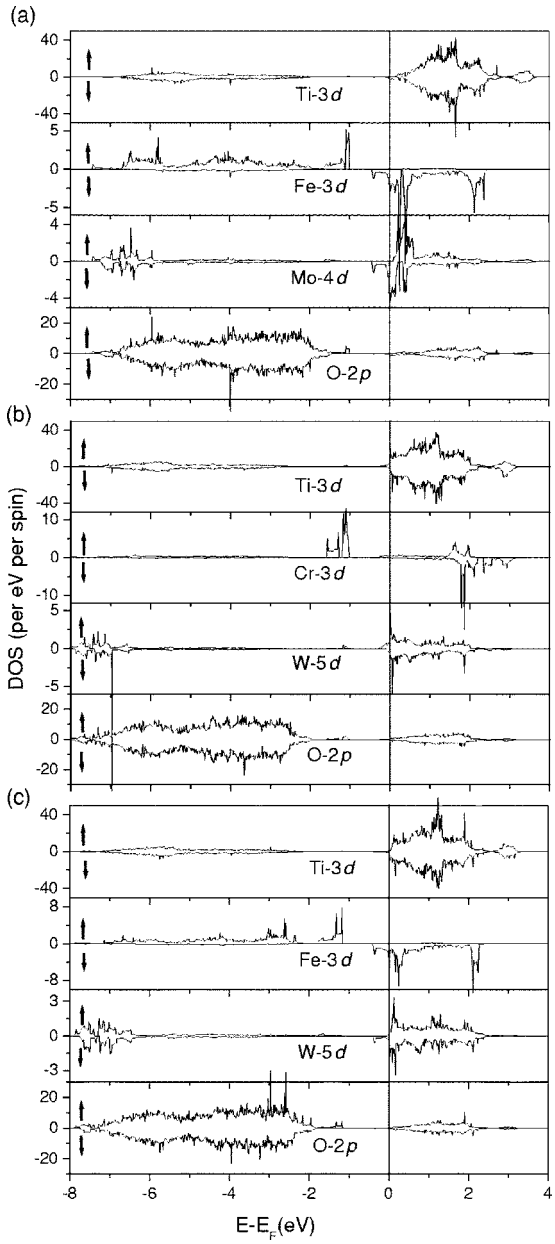

FIG. 2. Partial DOS of Ti-3d, M_1-3d, M_2-4(5)d, and O-2p of (a) M_1=Fe and M_2=Mo, (b) M_1=Cr and M_2=W, and (c) M_1=Fe and M_2=W are shown. The up and down arrow indicate the majority and minority spin states. The strong p-d hybridization between the Ti or impurities with oxygen atoms are also seen from this figure.

TABLE I. The energy separation between CBM and the highest occupied impurity states (M_1 and M_2, and nature of system (NS) are given for double-impurities-doped TiO_2 (rutile). The metallic, half-metallic, and semiconducting nature are shown as *M*, *H*, and *S*, respectively. "a" means all states are unoccupied.

	Energy separation (eV)								
	Mo			W			Re		
M_1/M_2	M_1	M_2	NS	M_1	M_2	NS	M_1	M_2	NS
Cr	0.77	0.13	*H*	0.94	−0.08	*M*	0.86	0.25	*H*
Mn	0.49	0.28	*H*	0.23	a	*S*	0.47	0.37	*H*
Fe	0.09	0.09	*H*	−0.03	−0.03	*H*	1.18	0.25	*H*
Co	0.73	0.12	*M*	0.22	a	*S*	0.95	0.24	*M*
Ni	1.35	a	*S*	1.20	a	*S*	1.04	0.38	*H*

thermal energy of electron at room temperature (~0.025 eV). Thus, the motion of charge carriers is restricted within these impurity states. In light of these results, it can be stated the choice of suitable impurity pairs is important to bring the highest occupied impurity states close to the CBM and thus increase the motion of charge carriers from impurities states to conduction band in the system.

Due to the overlapping of the impurity states with the conduction band in Fe-W-doped TiO_2, some of charge carriers are accumulated around the Ti atoms (Fig. 3). In the Fe-Mo-doped rutile, both the impurity states are matched, although they are quite far away from CBM. The separation between the impurity states and the CBM may be explained based on the fact that the 4*d* orbitals of Mo are less broad than the W-5*d* oribitals. The oxidation states (OS) of Fe and W impurities in TiO_2 are measured roughly from the carrier's occupancy in the *d* oribitals [Fig. 2(c)]. OS for Fe and W are +2 and +6, respectively, most likely. The total and local moments of Fe and W are found to be 4.04, 3.70, and $-0.08\mu_B$, respectively. The local moment of impurities are quite far from the moments predicted by the ionic model. This can be explained by the covalent binding between the impurities and host.[18] We extended our calculations to a larger supercell of TiO_2 rutile containing two magnetic complexes (Fe-O-W), in order to understand the interaction between such complexes. The calculations showed that the magnetic complexes are preferably located far from each other, in the [110] plane. The results also showed that the ferromagnetic interaction between the complexes is favored by 12 meV over the antiferromagnetic case. Even though this energy difference is very small; it is possible that larger energy differences occur when defects are introduced in the Fe-W-doped TiO_2 rutile.

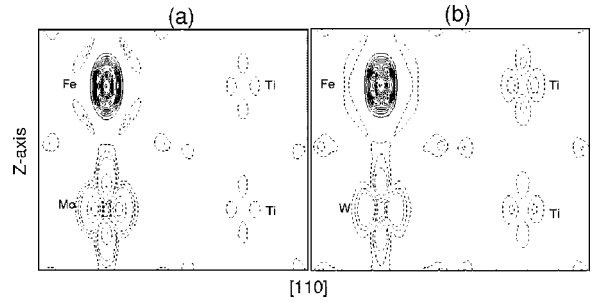

FIG. 3. Pseudo-spin-density contours (similar intervals) for (a) $Ti_{14}FeMoO_{32}$ and (b) $Ti_{14}FeWO_{32}$. The continuous and dotted contours mean the up- and down-spin components. The impurities states overlapping with the Ti conduction band are clearly depicted the presence of larger spin-density contours around Ti in $Ti_{14}FeWO_{32}$.

In summary, we have performed first-principles calculations on the double-impurities-doped TiO_2 to investigate the optimization of the conditions required for the synthesis of efficient spintronic devices. In this paper, we observe that the double impurities most likely substitute adjacent Ti sites and form stable magnetic complexes with the oxygen atoms. The results also indicate that by selecting suitable impurity pairs it is possible to develop systems where the highest occupied impurity states overlap well with the CBM. We observe interesting scenarios for developing spintronic devices using Fe-W-doped TiO_2. Since, the CBM is dominated by the minority spin electrons in this system; it can be used as electrical spin injectors to III-V semiconductor heterostructures.[19]

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